

ELECTRODE DESIGNS AND CONCEPTS FOR BIPOLAR ALKALINE FUEL CELLS

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Abstract—Fuel cells as direct energy converters and their economic applications in a future hydrogen economy are discussed briefly. Emphasis is put on the merits of a new way to construct and mass-produce alkaline fuel cells, eliminating the traditionally used expensive metal screens and porous nickel plaques and replacing them with plastic-bonded conductive materials for structures and porous carbons for electrodes.

Carbon electrodes have been used successfully in many types of fuel cell systems. Multi-layered thin carbon electrodes of high power output and long life can be produced by pressing, rolling and spraying methods.

Acetylene black, furnace blacks and graphites are used as carbon materials, mixed with PTFE and filler materials and evaluated in electrodes which are tested in laboratory cells, before they are built into stacks.

Compositions of the different mixtures for the fabrication of the electrodes are given and the advantage of the bipolar cell design from the construction and operating points of view is discussed.

INTRODUCTION

One of the most efficient means of generating power from hydrogen is the use of fuel cells as direct energy converters [1]. A fuel cell battery is an electrochemical device which converts the free energy change of a chemical reaction directly into electricity. There is no high-temperature combustion process involved in the conversion scheme and, therefore, Carnot's law, which limits the conversion efficiency of heat engines, is not applicable. The efficiency of conversion is therefore very high: under practical conditions 50-65% efficiency are achieved with a hydrogen-air fuel cell, compared to 15-25% with an automotive-type gasoline or diesel engine converted to operate on hydrogen as a fuel.

A fuel cell will operate as electrochemical generator as long as fuel and oxidant are supplied to the respective electrodes and as long as the reaction product (water vapor in the case of an hydrogen-air system) is continually removed. This feature is common with engines, but different from batteries, which have all the energy storing chemicals within their plates. Batteries may be discarded when exhausted (throwaway-type primary cells) or can be electrically recharged after being discharged (secondary cells or accumulators). The fuel containers of fuel cells are usually refilled within minutes, accumulators need hours for recharging.

The use of hydrogen as 'Universal Fuel' has often been discussed. It is certainly an ideal choice for some countries with plenty of water- or nuclear power available. It is also attractive for the storage of electrical

energy produced from alternate sources (hydrogen as universal 'energy currency' [2]).

Alkaline hydrogen-air fuel cells are especially suited for the use of clean hydrogen, e.g. produced by water electrolysis. Alkaline fuel cells have traditionally been constructed like batteries with plates, with current leads on the side or top and series or parallel-connected stacks. For a low cost production this principle must be changed to the 'bipolar' concept—discussed extensively below. Furthermore, the most expensive components in previous alkaline cells, the screens or porous backing plates made from nickel or silver must be replaced by porous carbon structures. The use of conductive plastic materials is essential to make larger fuel cell batteries mass-produceable. All major aspects of carbon technology are therefore important.

The carbon material selection is of prime importance. High chemical stability, good electrical conductivity, a medium-large surface and a suitable pores-distribution are required.

(1) The selection will tend to go in the direction of the carbon blacks; gas activation and heat treatments will be favourable. Carbon deposited from the gas phase with suitable catalysts under reproducible conditions have a good chance of succeeding.

(2) The electrode design must provide for several layers, which have different roles. Both, calandered or sprayed layers have been successfully made in the past.

(3) The binding agent (PTFE suspension) must be properly mixed, aged, combined with the right amount

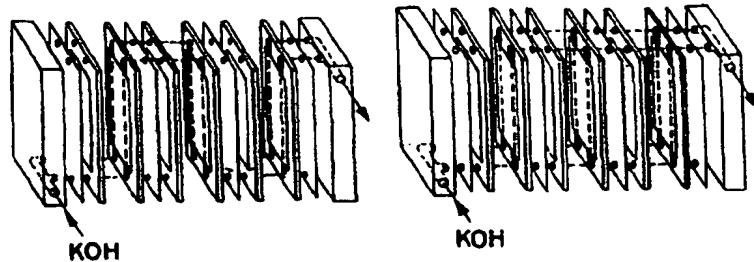


Fig. 1. A fuel-cell battery stack, designed for circulating electrolyte with bipolar cell design (Union Carbide). Left side: series flow, right side: parallel flow of electrolyte.

of wetting and sizing agent to adjust the agglomeration behaviour of the carbon-PTFE mixture in presence of different ions and at very accurate pH-values. The sintering of the PTFE must be controlled carefully to arrive at a repellent, but not overly wetproofed carbon surface. The use of (fine) PTFE-powder with fillers is a means for gaining porosity after their removal. Rolling (stressing) PTFE-bonded carbon layers creates cross-linkages and improves mechanical strength.

(4) The catalyst can only be efficiently used when it is highly concentrated on the surface. There are many application methods, but each must result in an even distribution of small catalyst agglomerates in good electrical contact with the carbon.

A weak point is, that many details with respect to the carbon processing steps are not sufficiently disclosed by the manufacturers or are not known to the electrochemist. A concerted effort by several laboratories to apply the same tests and techniques and then compare the results, would help.

An 'International Common Samples' approach, would be useful. The manganese dioxide battery business has profited from such an approach [3].

The carbon materials [4] can be selected from CTO-lampblack, heat treated acetylene-blacks (Shawinigan, GULF) and commercial furnace blacks (Vulcan XC, Carbot, Ketjenblack, etc.). All carbon materials which are used in 'active layers' should be subjected to high-temperature steam, CO_2 , or ammonia. These treatment processes (especially in the presence of Co-Al-spinels or heavy metal catalysts increase the carbon surface, oxidize the unstable carbon and could deposit new pyrolytic carbon. Experiments proved, that this is happening on carbon surfaces in the presence of traces of heavy and noble metals like Co, Fe, Pt, etc. The 'new' carbon can support current densities up to 4 A cm^{-2} and is quite stable.

The functioning of a noble metal catalyst depends on its surface area and on its substrate. The decomposition of Pt-salts is one of the preferred methods of applying the electrocatalyst to the supporting carbon.

Difficulties arise with the presence of the plastic binders, especially with structures of PTFE: catalyst deposited on the binder is useless and wasted. Catalyst

deposited on the wetproofed surfaces (Paraffin, Polyethylene) reduces the hydrophobicity. To solve these problems, the catalyzing noble metal solutions were mixed with isopropylalcohol, which can easily be removed later [5].

BIPOLAR ELECTRODES

This type of electrodes has always been used in phosphoric acid cells. In order to reduce the voltage drop on the internal resistance and to avoid expensive metal collector structures like porous nickel screens, bipolar designs for alkaline cells are now under investigations at our institutes.

Figure 1 shows a fuel cell battery stack, designed for circulating electrolyte, using extruded and baked porous carbon plates, or moulded carbon-plastic electrodes [6]. In stacks of that kind the contact with the bipolar centre plate (usually a thin sheet of nickel) was made with nickel or silver screens or nets.

Figure 2 shows the electrode arrangement in alkaline bipolar cells (left side) to be compared with the construction of cells with edgewise contacted electrodes. Type P_1 represents the situation described in Fig. 1. The right side of the drawing shows the possible use of the same electrodes in the monopolar contact arrangement. The contact plate P_2 consists of a plastic-carbon compound which has sufficient conductivity (in the range of $0.01-0.1 \Omega \text{ cm}$) to allow the elimination of the nickel screen contacting member. Combined with low-cost electrodes, mass-produced, this seems to be the future way to produce fuel-cell stacks for electric vehicles [7] and power plants [8].

PRODUCTION AND TYPES OF ELECTRODES

The production steps which are presently used to manufacture multiple-layer carbon electrodes from PTFE-powders and PTFE-suspensions are all related to each other. When pressed into a metal screen, the electrodes can be used in alkaline electrolytes. When supported on a carbon paper, they are suitable for acidic cells. Noticeable are the different ways to produce the 'backing layer' (with PTFE and acetylene-black, using

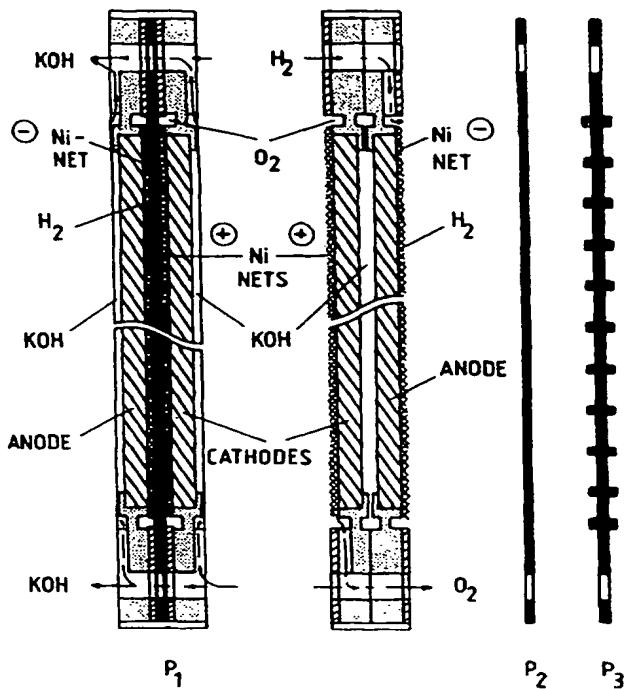


Fig. 2. The electrode arrangement in alkaline bipolar cells (left side) to be compared with the construction of cells with edgewise contacted electrodes. Type P₁ represents the situation described in Fig. 1. The right side of the drawing shows the possible use of the same electrodes in the monopolar contact arrangement. The contact plates (type P₂ or P₃) consist of a plastic-carbon compound which has sufficient conductivity (in the range of 1.0-0.1 Ω cm) to allow the elimination of the nickel screen contacting member.

ammonium carbonate as a pores-builder), the 'gas-diffusion layer' (from a mixture of active carbon and PTFE-suspension) and the 'catalyst-layer' (from graphite, sugar, Pt-black and PTFE-powder). Of course, there are also other combinations [9].

At the Institute for Inorganic Chemical Technology of the Technical University of Graz the following manufacturing methods were used to produce three types of electrodes for fuel cells [10]:

Type A: for alkaline electrolytes

Two- or three-layered electrodes with terminal-(tab)-current collection, with the use of nickel-plated steel screens or nickel nets as collectors. As protection against the penetration of electrolyte a porous PTFE-foil is sintered onto the gas side of the electrode. These electrodes can only be used in monopolar cells.

The construction scheme is as follows:

Pt-catalyst on carbon, 5-15% PTFE
carbon with 15-40% PTFE, nickel screen
(porous PTFE-foil).

Type B: for alkaline electrolytes

Two- or three-layered electrodes with terminal-(tab)-current collection, with the use of nickel screens or expanded metal as collectors situated in the diffusion-layer.

The construction scheme is the following:

Pt-catalyst on carbon, 5-15% PTFE
carbon with 15-40% PTFE
nickel-mesh (with graphite and 40-60% PTFE, sintered).

Type C: for alkaline and acidic electrolytes

A three-layered electrode for exclusive use in bipolar cells.

The construction scheme is the following:

Pt-catalyst on carbon, 5-15% PTFE
carbon with 15-40% PTFE
carbon-fleece (carbon paper) or carbon cloth with 40-60% PTFE.

All three types of electrodes can also be used as hydrogen electrodes [11]. In this case platinum is replaced by a mixture of platinum and palladium or rhodium and palladium (20:80). The catalyst metals are applied to the surface the carbon by impregnation with the corresponding aqueous solutions of their salts [12].

The methods for the production of individual layers of the electrodes are listed below in an outline of fabrication processes:

MANUFACTURING PROCESSES

(1) Rolling or calandering a mixture of carbon, PTFE-powder and suspension agent, e.g. a light fraction of petrol or toluene. The addition of a filler (sugar or bicarbonate) for establishing of pores is optional.

(2) Pressing of a mixture of carbon (with or without catalyst) with a filler and PTFE-powder.

(3) Spraying of: (a) a very diluted aqueous suspension of PTFE, mixed with carbon powder (with or without catalyst). The ratio between carbon and PTFE is determined by weight and the dilution of the viscous mixture is adjusted to the spraying device; (b) a mixture of carbon powder (with or without catalyst) and polyethylene powder dissolved in a solvent like toluene, xylene or tetrachloroethylene [13, 14].

A combination of all three methods is advised in certain cases, e.g. a very thin catalyst-carbon layer can be rolled, and a diffusion layer can be sprayed on top of it. A porous PTFE-foil may be pressed onto the gas side of the electrode to prevent electrolyte penetration through the structure into the gas manifold. All multi-layer electrodes must be pressed or slightly rolled and sintered at about 300°C for approximately 20 min. Additional wetproofing [15] is advised, because PTFE is not small enough to penetrate the small pores.

The catalyst can either be a commercially available platinum black which is mixed with the carbon, or it can be purchased already deposited on the carbon (e.g.

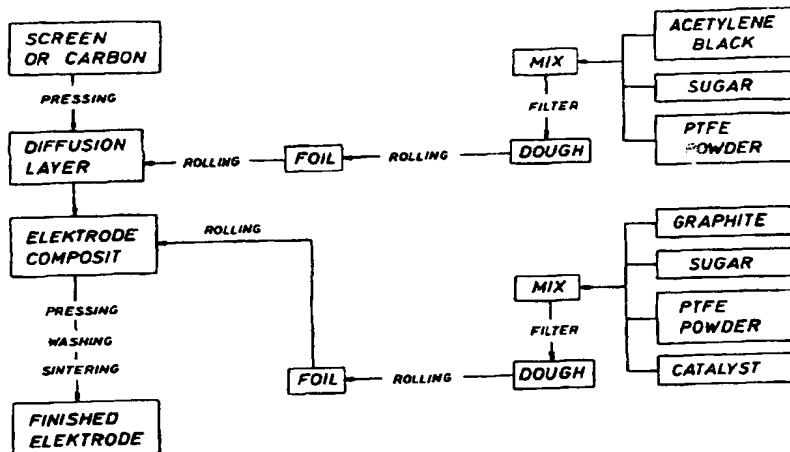


Fig. 3. Example for a flow diagram of the electrode production following the rolling method (M. Schautz).

10% Pt on Vulcan XC-72). Another method of applying the catalyst to the surface of the finished electrode is the brushing or printing of the platinum-salt solution in exact concentration onto the electrode. A squeegee as used in photographic work is very useful for that purpose. The active catalyst metal is then produced by thermal or chemical reduction of the dried salt. The work of M. Schautz [16] dealt with the optimization of the production methods for rolled electrodes (Type A). He was concerned with the following parameters:

The carbon material used,
the weight percentage of PTFE,
the choice and amount of filling material,
the composition, amount and method of application
of the catalyst and the sintering conditions.

An example of a flow diagram for the electrode production utilizing the rolling method is shown in Fig. 3. A comparison of electrodes produced in accordance with the rolling method is given in Table 1.

Jahangir [17] investigated the manufacturing of electrodes following the procedures for pressing electrodes in accordance with scheme B. Figure 4 shows the flow sheet for the production of electrode with ammonium carbonate as filling material in the diffusion layer. The active layer is manufactured by binding the carbon material with aqueous PTFE-suspension (Teflon B-30, a product of DuPont, containing 60% solides).

Table 2 compares the different electrodes produced by pressing the layers. All these electrodes have been catalyzed by the application of Pt-salt solutions to a

Table 1. Electrodes produced in accordance with the rolling method (M. Schautz)

Element No.	Diffusion zone	Catalyst zone	Catalyst (cm^{-2})	Voltage, R-free, vs Zn		
				100 mA (cm^{-2})	200 mA (cm^{-2})	Operation with air
12	Shawinigan 60% PTFE 16% Sugar 24%	Vulcan 45%	0.5 mg Pt	24 h	1.31	1.26
		PTFE 7%		100 h	1.26	1.22
		Sugar 44%	4% Platin	200 h	1.22	1.17
17	Vulcan 25% PTFE 12% Sugar 60%	Vulcan 45%	0.5 mg Pt	24 h	1.32	1.27
		PTFE 7%		100 h	1.29	1.22
		Sugar 44%	4% Platin	100 h	1.29	1.22
33	Shawinigan 25% PTFE 15% Sugar 60%	Acetogenobl. 73%	0.4 mg Pt	24 h	1.36	1.33
		PTFE 8%		130 h	1.28	1.25
		Sugar 17%	2% Platin	200 h	1.31	1.27
				500 h	1.29	1.24
38	Shawinigan 25% PTFE 15% Sugar 60%	Ketjenblack 68%	0.4 mg Pt	24 h	1.31	1.25
		PTFE 14%		200 h	1.33	1.25
		Sugar 15%	3% Platin	500 h	1.29	1.24

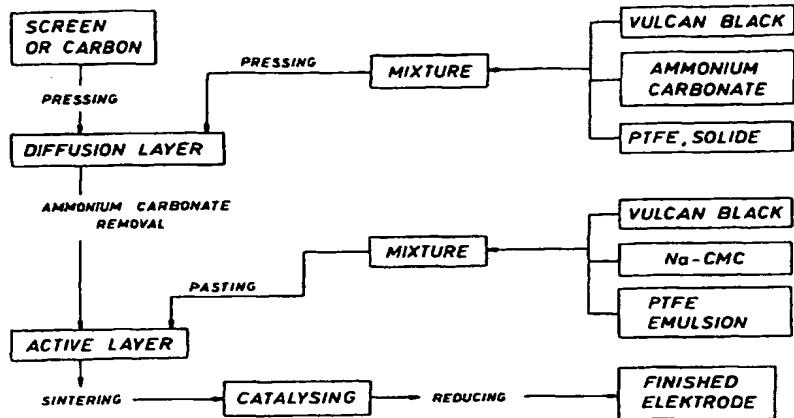


Fig. 4. The flow sheet for the production of electrodes with ammonium carbonate as filling material in the diffusion layer (S. Jahangir).

level of 0.5–1.0 mg Pt cm⁻² [18, 19]. They were pressed at 50 kg cm⁻² and sintered at 320°C for 20 min in nitrogen atmosphere.

The production of sprayed electrodes in accordance with scheme C is presently being investigated by K. Kordes and J. Gsellmann at the Institute for Inorganic Technology at the Technical University Graz. Parallel work on carbon electrodes is being conducted by K. Kordes and S. Srinivasan at the Institute for Hydro-

gen Systems in Toronto, Canada in order to establish a pilot-scale production.

Scheme C contains the essential steps for the fabrication of multi-layer PTFE or PE (polyethylene)-bonded carbon electrodes for bipolar fuel cell electrodes. Control of the sprayed amount of carbon and plastic is assured by the composition and the weight of the dried layers. The quantity of the solvent or diluent does not matter, because it is vaporized.

Table 2. Electrodes produced in accordance with the pressing method (S. Jahangir)

El. No.	Diffusion Zone	Active Zone made without Pt (added later)		Voltage, R-free, vs Zn 100 mA cm ⁻² 200 mA cm ⁻² Operation with air			
		21%	25%	20%	1 h: 200 h:	1.18 1.23	1.07 1.09
20	PTFE-Powder Vulcan (NH ₄) ₂ CO ₃	21%	PTFE-Emulsion Vulcan	20% 80%	1 h: 200 h:	1.18 1.23	1.07 1.09
7	PTFE-Powder Ketjenblack (NH ₄) ₂ CO ₃	12% 28% 60%	PTFE-Emulsion Ketjenblack	20% 80%	1 h: 200 h:	1.27 1.27	1.24 1.21
58	PTFE-Powder Acetylene Bl. (NH ₄) ₂ CO ₃	21% 25% 54%	PTFE-Emulsion Acetylene Bl.	20% 80%	1 h: 200 h:	1.15 1.12	1.04 1.02
85-89	PTFE-Emulsion Steam/CO ₂ activated Vulcan XC-72 or Steam/CO ₂ activated Acetylene Bl.	20% 80% 80%	Double layer design (a) PTFE-Powder CO ₂ or steam activated Acetylene Bl. (NH ₄) ₂ CO ₃ (b) PTFE-Powder CO ₂ or steam activated Acetylene Bl. (NH ₄) ₂ CO ₃	20% 20% 60% 12% 28% 60%	1 h: 200 h: 2500 h	1.27 1.26 1.22	1.23 1.18 1.10

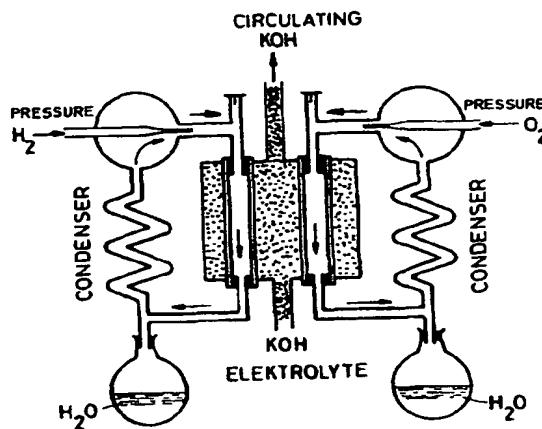


Fig. 5. A test set-up for working with different gas mixtures and under controlled temperature-, humidity- and flow conditions. The circulation is attained by two jet-circulation devices.

Example 1: Stackpole carbon-fleece (paper) is impregnated by spraying with Teflon B-30 in order to use it as a porous hydrophobic current collector for bipolar

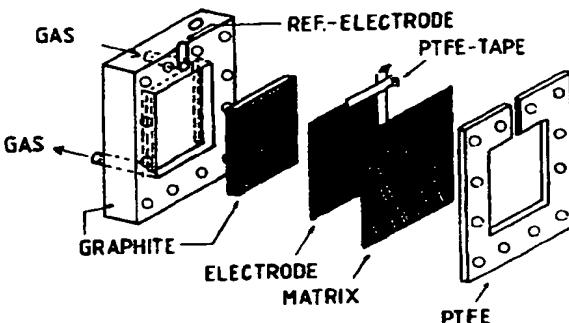


Fig. 6. Experimental test set-up for a Matrix Cell to be used with immobilized alkaline and acidic electrolytes.

electrodes. The active layer is produced on top of the carbon paper by spraying with a suspension of carbon in a 5% solution of polyethylene in tetrachloroethylene (b.p. 121°C). The spraying is performed at elevated temperature (60–90°C). Depending on the spraying device the viscosity of the suspension is adjusted by further dilution.

Example 2: The Teflon-impregnated carbon paper is

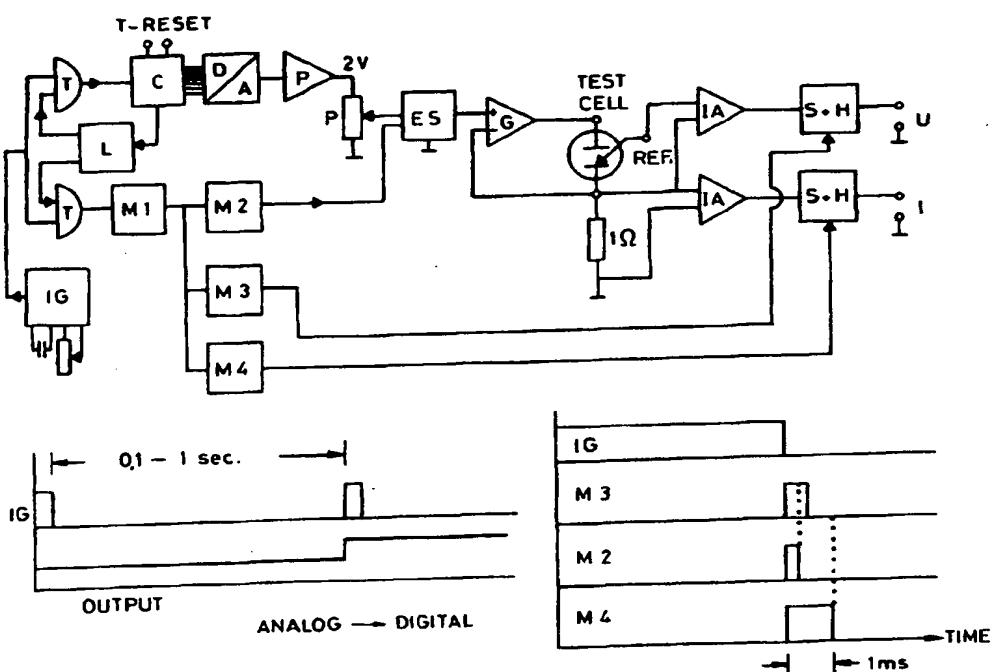


Fig. 7. A measuring circuit for the determination of resistance-free voltages under load conditions (J. Gsellmann). The device interrupts the current for e.g. a millisecond each second and holds the voltage in a sample and hold circuit. (IG) I-Pulse Generator, (C) Counter, with 'Reset', (L) Logic, triggering (T), (D/A) Digital to Analog transfer, (P) Potentiometer, (ES) Electronic switch, (M1, M2, M3, M4) Mono-vibrators, (IA) Instrument-amplifier, (S&H) Sample and Hold Circuit.

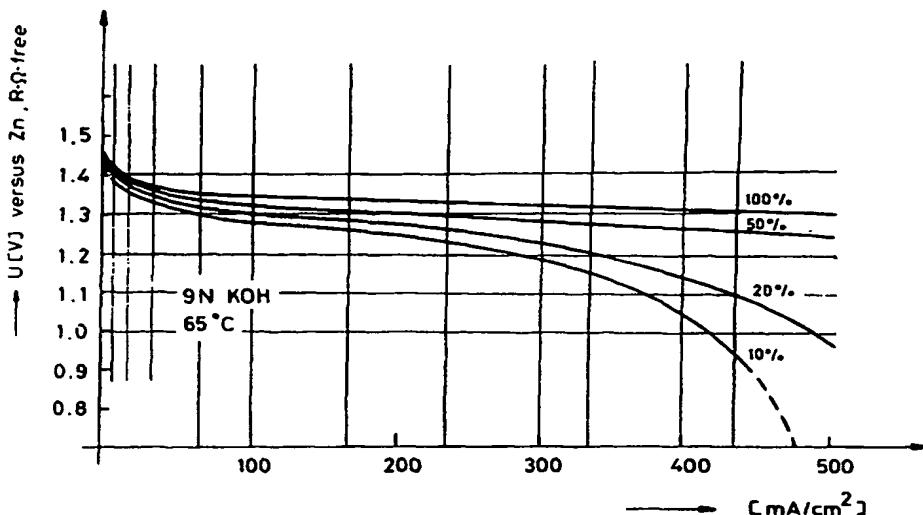


Fig. 8. Resistance-free polarization curves of electrode No. 33 (Table 1). The difference between O_2 and air performance is significant.

sprayed with a suspension of carbon (e.g. Vulcan XC-72) in aqueous emulsion of Teflon B-30. It should be noted that some carbon materials change the pH-value of the mixture, which may cause a flocculation of the PTFE. To minimize this effect about 3–6% triton X-100 (Rhom & Haas) are added.

ELECTRODE EVALUATION

Electrode evaluation of low-temperature alkaline cells must be done under well known conditions of temperature and humidity. Calculations have been made about the best ways to remove the water produced, either through a jet-recirculation/condensing loop on the hydrogen side, utilizing the high heat transfer value of this gas, or through an increased flow rate of dry air (from the CO_2 -absorber).

Figure 5 shows a test set-up [20] for working with different gas mixtures and under controlled temperature, humidity and flow conditions. The gases are circulated by means of gas-jets [21, 22]. Figure 6 shows the experimental set-up for Matrix Cell.

PERFORMANCE TESTING

Performance testing analyses the polarization behaviour of the manufactured anodes and cathodes. Data available to day are encouraging: the characteristic long-life performance is already in thousands of hours. The resistance-free [23] voltage difference between oxygen and air performance is used as a measure of the deterioration during ageing. A new measuring circuit for the determination of resistance-free voltages under load conditions was developed (see Fig. 7).

As an example of the performance of PTFE-bonded

carbon electrodes produced in accordance with one of the described production methods, the resistance-free polarization curves of electrode No. 33 are shown in Fig. 8.

TECHNICAL SUMMARY—CONCLUSIONS

The carbon material selection is of prime importance. PTFE as a binder can be used as powder or as aqueous emulsion. Multi-layer designs are optimal for fuel-cell electrodes. Removable fillers serve as adjusters for the porosity of layers. The bipolar concept is suitable for acidic and alkaline systems. Electrode fabrication steps include: pressing, rolling and spraying. The catalyst application methods are adaptable to production methods. Conductive plastic is a low-cost construction material. Extrusion of frames and plates are mass-production methods.

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